

ATRP OF VINYL MONOMERS BY CYCLOMETALATED Ru(II) COMPLEX WITH LABILE LIGANDS AND SnCl₂ AS A REDUCING AGENT.

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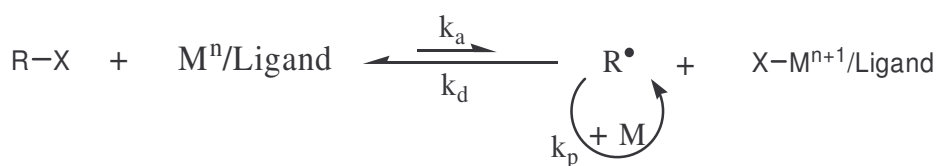
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Abstract. Atomic Transfer Radical Polymerization (ATRP) of n-butyl acrylate, methyl methacrylate and styrene were induced via a new cyclometalated Ru(II) complex with formula [Ru(Phpy)(MeCN)₄]⁺PF₆⁻. Such complex has MeCN labile ligands. Initially the mechanism by which the polymers were obtained (PBA, PMMA and PS) behaves as a free radical polymerization with poor control over both molecular weight and polydispersity (PDI in a range 1.7-2.0). SnCl₂ (reducing agent of the Ru(III) species formed in the first stage) was added in different concentration (from 0.1 to 0.5 mol) to the polymerizations systems to improve catalyst performance. Best results were obtained at SnCl₂ concentrations in a range of 0.3 to 0.5 mol. Substantial improvements over the control of both molecular weight and polydispersity were observed (PDI decreased until 1.15-1.2). The reaction mechanism corresponds to a living/controlled radical polymerization.

Introduction

Since the pioneering works of M. Sawamoto and K. Matyjaszewski at the beginning of the 90's years, atom transfer radical polymerization (ATRP) has progressed enormously to become one of the most efficient methods to prepare polymers with predictable molecular weights and narrow polydispersity (close to or even less than 1.1).^{1 to 6}. The method has been applied to a wide range of the monomers including styrenes, methacrylates, acrylamides, etc. and the polymerization may be conducted in bulk, solution or emulsion.

The key reaction herein is the reversible homolysis of a carbon-halogen bond of an alkyl halide initiator by a metal catalyst (see scheme 1).



Scheme 1

In this process the metal complexes undergo single electron oxidation into a higher state via the abstraction of the halogen from the target species. Thus the metal complexes should be able to receive a halogen and they should be easily oxidized and the oxidized form should be able to be easily reduced to the original state. In order to suppress the termination and also to give an equal opportunity of propagation for all polymer chains, the reversibility should be very fast and the equilibrium should be significantly shifted to the left ($k_d \gg k_a$) allowing the dormant species to dominate in the system. Therefore, it is preferable that the reduced or original state of the metal complexes should be more stable than its higher oxidation state. If the latter is not true and the metal prefers to stay in the higher oxidation state, the catalysts may be very active but control of the polymerization is poor and the process proceeds rather as an ordinary free radical polymerization.

Until now no general theory exists which can predict the activity of the catalysts, but it is commonly accepted that complexes with lower redox potentials demonstrate higher activity. The catalysts activity in each specific case can be tuned by changing the ligands of the complexes. A number of transition metals have been investigated as catalysts for ATRP, such as Cu, Ru, Fe, Ni, etc. together with a variety of ligands. Among these the Cu and Ru compounds are the most frequently used for this purpose. Cu catalysts are the most extensively studied while for others the process mechanism is still not so well established.

Ru(II) compounds for ATRP were first introduced by M. Sawamoto and now they are the second most frequently used catalysts. Thanks to its position in the periodic table Ru possess one of the richest chemistry among all transition metals.⁷ Variety in the complexes structures and ligands options for Ru are enormous and much greater than for Cu. Since the reactivity of the catalysts is tuned by the ligands, the Ru compounds are some of the most interesting materials. Unfortunately relatively few of the existing Ru complexes have been actually tested for ATRP. Thus these complexes are worthy of study to try to find new catalysts of higher activity or that are capable of providing controlled polymerization of monomers which are still problematic to polymerize using existing approaches.

Recently synthesis and properties of a series of new cyclometalated Ru (II) complexes⁸ have been reported. Some of them have labile ligands and demonstrate relatively low redox potentials. Taking into account all these together with the highly effective and simple synthetic route,^{9,10} we considered that it would be interesting to verify these complexes as catalysts for ATRP. Hereby, we report the application of one of such complexes, $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-$ for the polymerization of butyl acrylate, methyl methacrylate and styrene. It is known that polymerization occurs only in the presence of Lewis acid, such as $\text{Al}(\text{iOPr})_3$.

Experimental Section.

Materials. Ruthenium (III) chloride hydrate was purchased from Strem Chemicals and was used as received. All others chemicals were purchased from Aldrich Chemical and also were used as received except the monomers (butyl acrylate, methyl methacrylate, and styrene), these first were washed with 1% w/w aqueous solution of NaOH to remove the inhibitor, dried over magnesium sulfate anhydrous and then distilled under vacuum to remove oligomers.

Analysis. Monomer conversions were determined gravimetrically. Molecular weights measurements and its distribution were done by gel permeation chromatography (GPC) using at Waters HPLC, model Alliance 2695 equipped with the next: refraction index detector model 2414; two ultra high resolution high speed columns HSPgel HR MB-L (500-700,000) and HSPgel HR MB-M (1000-4,000,000) thermosetting at 35°C. For poly-butylacrylate and poly-methylmethacrylate a calibration curve made with polymethylmethacrylate standards at 10 points (2580, 10100, 31600, 54500, 93300, 158000, 267000, 460000, 701000 and 981000) was used. Molecular weights measurements of polystyrene samples were made with a calibration curve built with polystyrene standards at 16 points (370, 474, 996, 2950, 6520, 9730, 17800, 43700, 103000, 188000, 462000, 778000, 1270000, 2630000, 3440000 and 4290000). In all cases THF was used as a mobile phase.

Synthesis. Ruthenium dimer was synthesized in a round bottom flask as a follow: ruthenium (III) chloride hydrate was added to the reaction flask, then was solubility in ethyl alcohol followed by the addition of 1, 4-cyclohexadiene. Reaction mixture was submerged in an oil bath and then carry out to reflux by one hour. After that time at brown-reddish solid was formed, separately and dried by filtration under vacuum.

The **ruthenium (II) cyclometalated complex** was synthesized as a follow: ruthenium dimer, KPF_6 , NaOH, acetonitrile and 2-phenyl pyridine were added to the reaction flask. The reaction mixture was submerged in a oil bath previously stabilized at 40°C and keep at that temperature for a least 17 hours. After that the ruthenium (II) complex formed was isolated by column chromatography using neutral alumina as a stationary phase and di-chloromethane as a mobile phase. The yellow solution obtained was concentrated by vacuum distillation until get a yellow solid.

Polymerizations (using SnCl_2 as a reducing agent) were carried out as a follow: ruthenium (II) cyclometalated complex, aluminum isopropoxide and reducing agent were put into a Schlenk flask. Oxygen and humidity (present in air) were remove by doing vacuum followed by inject argon simultaneously many times. Then, monomer was added, stirrer until get homogeneous solution. After that, initiator was injected. Polymerization started when reaction mixture was submerged in an oil bath previously stabilized at reaction temperature. Samples were taking out at different times via a syringe. Polymerization stopped when reaction mixture got very viscous. Molar ratios for each polymerization systems were: monomer (200) / initiator (1) / Ru complex (1) / Al isopropoxide (1) / SnCl_2 (from 0.1 to 0.5) respectively.

Molar concentration:

Butyl acrylate (6.9517) / MBP (0.0347) / $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-$ (0.0347) / Al iso. (0.0347) / SnCl_2 (from 0.0034 to 0.017) mol/liter respectively

Methyl methacrylate (9.3506) / EBiB (0.0467) / $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-$ (0.0467) / Al iso. (0.0467) / SnCl_2 (from 0.0046 to 0.023) mol/liter respectively

Styrene (8.7278) / BEB (0.0436) / $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-$ (0.0436) / Al iso. (0.0436) / SnCl_2 (from 0.0043 to 0.0215) mol/liter respectively

Where MBP=Methyl-2-bromopropionate; EBiB= Ethyl-2-bromoisobutyrate; BEB= (1-Bromoethyl)-benzene.

Results and discussion.

Table 1. Molecular weights, polydispersity, and conversion for ATRP of n-butylacrylate using $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-$ as a catalyst and SnCl_2 as a reducing agent. Concentrations: $[\text{n-butylacrylate}]_0=6.9517\text{ M}$; $[\text{MBP}]_0=0.0347\text{ M}$; $[[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-]_0=0.0347\text{ M}$; $[\text{Al}(\text{iOPr})_3]_0=0.0347\text{ M}$; $[\text{SnCl}_2]_0=$ from 0.0034 to 0.017 M, $T=80^\circ\text{C}$

| Deactivator/ concentration | Time (hours) | Conv. (%) | Mn (teo) 1×10^3 | Mn (exp) 1×10^3 | PDI |
|-------------------------------|-----------------|--------------|-----------------------------|-----------------------------|------|
| without | 0.5 | 20.0 | 4.2 | 67.0 | 2.37 |
| | 1.0 | 76.0 | 16.0 | 68.4 | 2.45 |
| $\text{SnCl}_2 / 0.1$ | 1.5 | 57.0 | 12.0 | 65.8 | 2.25 |
| | 2.0 | 79.0 | 17.0 | 66.2 | 2.21 |
| $\text{SnCl}_2 / 0.2$ | 1.5 | 53.0 | 11.1 | 62.1 | 1.93 |
| | 2.0 | 73.0 | 15.3 | 72.7 | 1.91 |
| $\text{SnCl}_2 / 0.3$ | 1.5 | 46.0 | 9.7 | 51.7 | 1.64 |
| | 2.0 | 68.0 | 14.3 | 58.7 | 1.58 |
| $\text{SnCl}_2 / 0.4$ | 1.5 | 41.0 | 8.6 | 42.4 | 1.35 |
| | 2.0 | 59.0 | 12.4 | 66.9 | 1.28 |
| $\text{SnCl}_2 / 0.5$ | 1.5 | 37.0 | 7.8 | 38.4 | 1.29 |
| | 2.0 | 51.0 | 10.7 | 62.3 | 1.21 |

In all BA polymerization trials the initial rate of reaction was very fast (up to 40% conversion), then it decreased until 60-65 % conversion was reached in about 4 h. However, the control of the molecular weight was poor. Experimental molecular weights were 4-5 times greater than predicted by theory. Polydispersity was high for the systems without SnCl₂ (2.45) but with SnCl₂ the polydispersity decreased down to 1.21 as concentration was increased. The first three runs, Table 1 (SnCl₂ concentrations 0.0, 0.1 and 0.2 mol) behaved as a free radical polymerization because the same molecular weight was obtained at any conversion. At SnCl₂ concentrations above 0.3, better control of the molecular weight and polydispersity was obtained, in these runs the molecular weight increased with conversion.

The ATRP of methyl methacrylate also were conducted at 80°C in bulk. Results are shown in Table 2. Big differences between experimental and expected molecular weights were observed (10-12 times greater) for all runs. At SnCl₂ concentrations above 0.3 mol, molecular weights increased linearly with the conversion and a better control on the polydispersity was obtained (PDI fall until 1.14). Conversion decreased as SnCl₂ concentration increased.

Table 2. ATRP of methylmethacrylate using [Ru(Phpy)(MeCN)₄]⁺PF₆⁻ as a catalyst and SnCl₂ as a reducing agent. Concentrations: [methyl methacrylate]₀= 9.3506 M; [EBiB]₀= 0.0467 M; [[Ru(Phpy)(MeCN)₄]⁺PF₆]₀= 0.0467 M; [Al(iOPr)₃]₀= 0.0467 M; [SnCl₂]₀= from 0.0046 to 0.023 M, T=80°C.

| Deactivator/ concentration | Time (hours) | Conv. (%) | Mn (teo) 1 x 10 ³ | Mn (exp) 1 x 10 ³ | PDI |
|-------------------------------|-----------------|--------------|---------------------------------|---------------------------------|------|
| without | 1.5 | 35.2 | 7.1 | 156.7 | 1.74 |
| | 2.0 | 53.6 | 10.8 | 178.5 | 1.73 |
| SnCl ₂ / 0.1 | 1.0 | 20.7 | 4.2 | 75.8 | 1.80 |
| | 2.0 | 32.3 | 6.5 | 76.2 | 1.79 |
| SnCl ₂ / 0.2 | 3.0 | 31.7 | 6.4 | 67.5 | 1.54 |
| | 4.0 | 35.7 | 7.2 | 92.7 | 1.53 |
| SnCl ₂ / 0.3 | 3.5 | 18.1 | 3.6 | 51.0 | 1.30 |
| | 4.5 | 24.3 | 4.9 | 59.0 | 1.29 |
| SnCl ₂ / 0.4 | 2.5 | 43.3 | 8.7 | 72.4 | 1.37 |
| | 3.0 | 61.6 | 12.4 | 86.9 | 1.36 |
| SnCl ₂ / 0.5 | 3.0 | 18.9 | 3.8 | 58.4 | 1.21 |
| | 4.0 | 24.4 | 4.9 | 62.5 | 1.14 |

Simultaneously molecular weights were dropped and started progressively enlarge with conversion and PDIs were more narrow. The best result for all the systems was observed when SnCl₂ concentration was equal half those of the catalysts. At this concentration molecular weights were still higher than the calculated values but they significantly dropped compare to those obtained with no SnCl₂ added and increased with conversion. The PDIs were as narrow as 1.15–1.2 depending on the system.

Table 3. ATRP of Styrene using $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-$ as a catalyst and SnCl_2 as a reducing agent. Concentrations: $[\text{Styrene}]_0 = 8.7278 \text{ M}$; $[\text{BEB}]_0 = 0.0436 \text{ M}$; $[[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-]_0 = 0.0436 \text{ M}$; $[\text{Al iso}]_0 = 0.0436 \text{ M}$; $[\text{SnCl}_2]_0 = \text{from } 0.0043 \text{ to } 0.0215 \text{ M}$, $T = 100^\circ\text{C}$.

| Deactivator/ concentration | Time (hours) | Conv. (%) | Mn (teo) 1×10^3 | Mn (exp) 1×10^3 | PDI |
|-------------------------------|-----------------|--------------|-----------------------------|-----------------------------|------|
| without | 3.0 | 60.5 | 12.7 | 29.2 | 1.67 |
| | 4.0 | 67.6 | 14.2 | 34.8 | 1.65 |
| $\text{SnCl}_2 / 0.1$ | 4.0 | 41.7 | 8.7 | 32.0 | 1.68 |
| | 24. | 81.2 | 17.0 | 45.1 | 1.68 |
| $\text{SnCl}_2 / 0.2$ | 4.0 | 34.9 | 7.3 | 28.4 | 1.66 |
| | 24.0 | 88.2 | 18.5 | 47.8 | 1.63 |
| $\text{SnCl}_2 / 0.3$ | 4.0 | 32.1 | 6.7 | 29.6 | 1.61 |
| | 24.0 | 54.7 | 11.5 | 32.2 | 1.59 |
| $\text{SnCl}_2 / 0.4$ | 4.0 | 27.9 | 5.8 | 44.9 | 1.59 |
| | 24.0 | 50.8 | 10.7 | 48.4 | 1.55 |
| $\text{SnCl}_2 / 0.5$ | 4.0 | 11.7 | 2.5 | 15.6 | 1.18 |
| | 24.0 | 38.4 | 8.1 | 30.9 | 1.15 |

Further increase in SnCl_2 did not lead to the process improvement and caused problems in solubility. It should be noted that none of the monomers was polymerized without the Ru(II) complex, using only SnCl_2 , initiator and $\text{Al}(\text{OiPr})_3$.

Conclusions

Ruthenium complex $[\text{Ru}(\text{Phpy})(\text{MeCN})_4]^+\text{PF}_6^-$ did induce the polymerizations of various vinyl monomers, unfortunately the polymerizations were observed only in the presence of $\text{Al}(\text{OiPr})_3$ and proceeded without control. However when reducing SnCl_2 was added the polymerizations started to demonstrate more control: molecular weights were reduced comparing with those initially obtained, they gradually increased with conversions and finally narrow PDIs were obtained.

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